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AD-A188 790

OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014-86-K-0305

TECHNICAL REPORT NO. 19

Thermal Oxide Growth on Silicon: Intrinsic Stress & Silicon
Cleaning Effects

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in

Symposium Volume of American Vacuum Society

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report #19	5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION UNC Chemistry Dept.	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research (Code 413)
6c. ADDRESS (City, State and ZIP Code) 11-3 Venable Hall 045A Chapel Hill, NC 27514		7b. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract #N00014-86-K-0305

8c. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street, Arlington, VA 22217	10. SOURCE OF FUNDING NOS.			
	PROGRAM ELEMENT NO.	PROJECT NO	TASK NO.	WORK UNIT NO

11. TITLE (Include Security Classification) THERMAL OXIDE GROWTH ON SILICON: INTRINSIC STRESS & SILICON

12. PERSONAL AUTHOR(S) CLEANING EFFECTS E.A. Irene

13a. TYPE OF REPORT Interim Technical	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Yr., Mo., Day) December 3, 1987	15. PAGE COUNT 36

16. SUPPLEMENTARY NOTATION

Symposium Volume of American Vacuum Society

17	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB. GR.	Silicon, Silicon oxide

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson	22b. TELEPHONE NUMBER (Include Area Code) (202) 696-4410	22c. OFFICE SYMBOL

DD FORM 1473, 83 APR   EDITION OF 1 JAN 73 IS OBSOLETE.

Thermal Oxide Growth on Silicon: Intrinsic Stress and Silicon Cleaning Effects

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Abstract

This paper summarizes the experimental results and discusses the implications of recent research on two topics related to Si oxidation: mechanical stress effects; and the influence of impurities on the Si surface. For stress measurement, a double beam optical technique is used to measure the strain in the Si substrate due to the film stress. An intrinsic SiO_2 stress is measured which increases with decreasing oxidation temperature. Controversy exists about whether the intrinsic stress affects transport of oxidant or the interface reaction; arguments for both views are presented. A combination of in-situ ellipsometry and contact angle measurements performed on a Si surface which is immersed in various liquid media has been successfully used to determine the role of HF in Si cleaning process. A fluorocarbon film was found to replace the removed SiO_2, and the fluorocarbon renders the Si surface hydrophobic and amenable to the growth of a high quality SiO_2 film for device applications.

Introduction

The clear trend in silicon Microelectronics processing is towards lower process temperatures (1,2). The motivation is to reduce the diffusion of dopants and thereby to protect diffused junctions and eliminate unwanted interface reactions. This issue arises directly from the industrial effort to reduce device size and thereby increase the level of integration. The impact on the Si thermal oxidation process is profound and several real scientific issues emerge. Firstly, the reduction in lateral size of individual devices on a chip also requires a reduction in the gate area, A, of MOS devices. As seen in equation (1), in order to maintain the same device operating characteristics, viz., the device capacitance, C, because of the reduction of A, the oxide film thickness, L_{ox}, must also be reduced since

$$C = KA/L_{ox} \qquad (1)$$

where K is the dielectric constant for the SiO_2 film. The scientific issue here is that the contemplated integration schemes have driven the thickness range for SiO_2 films to below 20 nm. However, based on many recent studies, the presently accepted oxidation model, the Linear-Parabolic, L-P, model (3-5), is considered to be inapplicable for dry oxidations below about 30 nm SiO_2 thickness. In fact the L-P model is usually derived to contain an offset, L_0, to avert the thin film regime below several tens of nm as:

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$$t-t_o = (L-L_o)/k_1 + (L^2-L_o^2)/k_p \qquad (2)$$

where L and t are the SiO_2 thickness and time, L_o and t_o
represent the small thickness region in L, t space which does not
fit the model, viz. the offset region, k_1 and k_p are the linear
and parabolic rate constants, respectively (5). The initial
regime, for $L< L_o$, is characterized by faster than usual
oxidation kinetics. Further scientific investigation is required
to determine the reasons why this regime is different from the L-
P regime. Impurities are known to have a profound effect on this
regime (6-8), and we will summarize some recent research in this
area that is aimed at an understanding of impurity effects on the
Si surface. Secondly, the required reduction in process
temperatures directly affects some SiO_2 film properties (9). In
particular, intrinsic film stress, σ_i, film density, ρ, Si-SiO_2
interfacial fixed charge, Q_f, and possibly Si-SiO_2 interface
states, Q_{it}, all increase with decreasing oxidation temperature
and all anneal to lower temperatures as depicted in Figure 1.
These properties may also affect the Si oxidation mechanism. In
this paper, some current research on impurity effects and
mechanical stress effects on the Si oxidation mechanism is
discussed. A recent review (ref. 10 and references therein)
presents a more complete picture of the silicon oxidation
problem. We commence with a summary of stress effects.

Stress Effects on Si Oxidation

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Stress Relationships

Two components of the residual film stress, σ, are discussed: thermal stress, σ_{th}, and intrinsic stress, σ_i, and these are additive as:

$$\sigma = \sigma_{th} + \sigma_i \qquad (3)$$

The thermal stress or thermal expansion stress is attributed to the difference in thermal expansion coefficients, $\Delta\alpha$, between the SiO_2 film and the Si substrate as:

$$\Delta\alpha = \alpha(SiO_2) - \alpha(Si) \qquad (4)$$

which when multiplied by the difference between the film growth temperature, T_{ox}, and stress measurement temperature T, $\Delta T = (T_{ox} - T)$ and then multiplied by Youngs modulus, E, divided by $(1-\nu)$ where ν is Poissons ratio for the film yields an expression for the thermal stress:

$$\sigma_{th} = \Delta\alpha \cdot \Delta T \cdot [E/(1-\nu)] \qquad (5)$$

It should be clearly understood that σ_{th} cannot affect the oxidation reaction itself, since from eqn. (5) $\Delta T = 0$ at $T = T_{ox}$ and thus $\sigma_{th} = 0$ at the oxidation temperature. For SiO_2 on Si, $\alpha(SiO_2) < \alpha(Si)$, hence $\Delta\alpha$ is negative and a compressive thermal stress results upon cooling from T_{ox} to room temperature, i.e.,

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$\sigma_{t\,n}$ is negative.   The higher $T_{0\,x}$, the larger would be $\sigma_{t\,n}$ as

measured at room temperature.   Measurements done with oxides

grown at high oxidation temperatures of 1000°C and above (11,12)

have yielded stress results which are totally consistent with σ =

$\sigma_{t\,n}$ (σ_i = 0), viz. with a numerical value from the above

expression for $\sigma_{t\,n}$ and a larger room temperature value for larger

$T_{0\,x}$ values. However, for oxides grown at lower oxidation

temperatures, evidence for a non-zero intrinsic component was

reported (13,14).   In-situ stress measurements at $T_{0\,x}$ (where $\sigma_{t\,n}$

= 0) have shown that σ_i is also compressive and increases with

decreasing $T_{0\,x}$ (i.e. oppositely to the temperature dependence of

$\sigma_{t\,n}$.   The origin for this intrinsic stress was proposed to be due

to the large molar volume change, ΔV, for the conversion of Si to

SiO_2 which is 120% or a factor of 2.2x (14-16).   The direction

and order of magnitude of this stress has been confirmed (17,18).

Film Stress Techniques

Before proceeding to a summary of the stress measurements

results, it would be useful to present a brief description of

several stress measurement methods recently applied to SiO_2

films.   Virtually all of the experimental measurements determine

the strain or the deformation in the substrate, as caused by a

thin uniform film on one surface of the substrate.   The strain is

directly proportional to stress in the elastic limit, and for the

case of the substrate thickness being much larger than the film

thickness, the film stress, σ_f, can be related to the radius of

curvature, R, of the substrate through Stoney's formula (19):

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$$\sigma_f = [E \cdot L_{s} / (6 \cdot (1 - \nu) \cdot L_f)] / R \qquad (5)$$

where the elastic constants are for the substrate which is
deforming and L_s and L_f are the thicknesses for the substrate and
film respectively. Thus the experimental techniques are aimed at
measuring R. Three general classes of measurements are routinely
found in the literature: mechanical, diffraction, and optical.
These differ in the manner in which R is measured and under each
general class usually several techniques have been developed. A
more complete discussion of film stress measurement will be
reserved for a separate review, and herein we discuss only
specific reports of stress in SiO_2 films on Si substrates. The
most recent reports have employed x-ray diffraction and optical
techniques (13,14,17,18).

One prominent x-ray technique is based on the maintenance of
the Bragg condition for diffraction from thin Si substrates
(21,22). Essentially, the single crystal Si substrate is brought
under Bragg conditions with respect to the incident x-ray beam,
through the use of major reflections for the specific Si
orientation used. While monitoring the diffracted radiation at
the Bragg angle, θ_B, the sample is traversed relative to the beam
while keeping the same angle to the beam. If the sample is
perfectly flat, the crystal planes remain with constant angles to
the x-ray beam and the Bragg conditions are maintained. If,
however, the Si substrate is curved as a result of film stress,

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then upon traversing the sample in front of the beam, the Bragg condition will be lost and an adjustment in the crystal position will be required to reattain the Bragg condition. The amount of adjustment depends both on the substrate radius of curvature, R, which is to be measured and the distance the sample is traversed which is known. This measurement apparatus is often automated and called ABAC for automated Bragg angle camera. The advantages of this technique is the great sensitivity to stresses as low as 10^7 dyne/cm^2 and absolute reference from the lattice planes in the single crystal substrate. The disadvantage is expense and complexity, as a high intensity x-ray source, diffraction camera, and associated automation apparatus are required.

A number of optical techniques have been used on SiO_2 films. One is the so-called Newton rings technique which makes use of the optical interference pattern caused by combining the reflections from the surface of an optical flat and a curved surface in contact with the flat (23,24). Using monochromatic light, a series of rings result, Newtons rings, the number of which in a certain distance, the separation, is proportional to the curvature of the surface, R. If very uniform surfaces are obtained, this technique can be useful for stresses of about 10^9 dynes/cm^2 and upwards. Cleanliness of the surfaces in contact is a problem as is obtaining flat or uniformly curved substrates for the measurements.

Two other optical reflection techniques have been reported. One technique uses the reflection of one narrow light beam from a

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film covered surface (see for example ref. (25)). The argument

here is that the reflected beam will be undeviated from a flat

surface which is traversed during reflection. If the surface is

curved, a deviation of the reflected beam will occur. As in the

ABAC case, the deviation can be geometrically related to R.

However, it is easy to show that a deviation due to curvature of

the substrate is difficult, if not impossible, to distinguish

from misalignment of a flat sample. Both situations would cause

reflected beam deviation. Thus, this technique is difficult to

use without unambiguous alignment procedures which, to this

authors knowledge, nave not been reported. The difficulty with

the single beam technique is obviated with the use of two

parallel reflected beams. An experimental apparatus is shown in

Figure 2 (17,18). The laser light is split (at BS1) then

reflected onto a silvered prism and adjusted so that the

reflected beams are parallel. The parallel beams are again split

(at BS2) with half going to a screen and forming two reference

spots of separation X. The other is reflected from the sample

surface, across the lab, in order to obtain a lever effect, and

then to another plane mirror (M3) and finally to the same screen.

If the sample is perfectly flat, the two sets of spots have the

same X separation; but if the sample is curved, then a different

separation, S, for the second set of spots is seen, viz. the

reflections from the sample. R is then easily calculated from

the difference between R and X and the measurement geometry.

This technique has the decided advantages of being able to

distinguish sample tilt from curvature, and to be absolutely

calibrated. For sample tilt, the two beams would be deviated in

a parallel fashion in one direction, but for curvature only the

spot separation changes. To insure beam parallelism, a flat

mirror is substituted for the sample and the apparatus in

adjusted such that the two sets of spots are identical. For

calibration of R, commercially available precision spherical

mirrors with known R replace the sample thus calibrating the

apparatus geometry. The results from this technique have been

found to be quite reproducible and are emphasized in the

discussion to follow.

SiO_2 Film Stress Results

The first studies of the SiO_2 film stress (11,12) were

performed using SiO_2 films grown at temperatures of 1000°C and

higher which were appropriate processing temperatures for that

era. These studies used predominantly mechanical measurements of

R and were concordant in that they reported residual room

temperature stress values that could be completely explained

based on the anticipated value for the thermal expansion stress

from equation (5) above. Hence, no evidence for an intrinsic SiO_2

stress was reported. From these studies, there was no reason to

include stress in any oxidation models, because at oxidation

temperature $\sigma_{t,n} = 0$. More recent results using a double beam

reflection technique in the Si oxidation environment, in-situ,

revealed that a compressive intrinsic stress exists at

temperatures less than 1000°C and this stress was found to

increase as the oxidation temperature decreased (13). This direction of change of the intrinsic stress with oxidation temperature is opposite to that anticipated for the temperature variation of the thermal stress as obtained from equation (5). Thus, this newly measured intrinsic stress is easily discerned even in the presence of the thermal expansion stress. Of course the in-situ measurement at the oxidation temperature insures that $\sigma_{t h} = 0$, hence no confusion results. More recent room temperature stress measurements using the ABAC technique (14) and the double beam reflection technique (17,18), have confirmed that an intrinsic SiO_2 film stress exists. Figure 3 shows a plot of total room temperature SiO_2 film stress measurements along with the calculated thermal expansion film stress resulting from equation (5) all as a function of the thermal oxidation temperature. The differences in the temperature variation for these two stress components is evident. Figure 4 shows σ_i which is the difference in the total and thermal stress against oxidation temperature. σ_i is seen to decrease with increasing oxidation temperature.

The origin and temperature dependence of σ_i is understood by considering the large molar volume change, ΔV, for the conversion of Si to SiO_2, and the viscoelastic nature of SiO_2 (14-16). From figure 5, we see that the as-formed SiO_2 occupies a greater volume than the Si from which it was produced, hence an expansion needs to occur into the free volume direction above the oxidizing Si surface. Using a Maxwell model for SiO_2, the rate at which the flow of SiO_2 can occur into this free direction is determined

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by the SiO_2 viscosity, η. At high oxidation temperatures where η is sufficiently small, the SiO_2 flows readily into the free direction with a short relaxation time relative to the time for oxidation. At lower temperatures, (below about 900°C), however, η is too large for complete relaxation, hence σ_i develops. The lower is T_{ox}, the higher is η, and the higher is σ_i. Relaxation time calculations seem to confirm this viscoelastic model for SiO_2 (14).

In terms of the relationship of σ_i to Si oxidation models, two different ideas have arisen. The first deals with the compressive σ_i in the SiO_2 film. This compression ought to reduce the diffusivity of O_2, hence the supply of O_2 to fuel the oxidation reaction. Thus a decrease in the oxidation rate should occur due to σ_i. Some confirmation for this exists from recent experiments (26) that show that when σ_i is released by long term annealing of thick SiO_2 films, the oxidation rate increases. Considering the molar volume change as the origin of σ_i, the stress distribution in the SiO_2 film should result in a large stress near the $Si-SiO_2$ interface with a decreasing stress towards the SiO_2 surface. This would result in a higher σ_i and a reduced oxidation rate for thinner SiO_2 films. However, it is well known that a higher oxidation rate is seen for thin films (less than 200Å), yet the shape of the thin SiO_2 oxidation data is explained by this model (27-29). Most recent σ_i measurements (20) have shown that indeed a higher stress exists for thinner films, but not as high as would be required from these diffusion

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models.

The second stress related oxidation model is derived from the fact that the compressive σ_i in SiO_2 gives rise to a tensile stress at the Si surface. The resulting strained Si bonds ought to yield a more reactive Si surface thereby enhancing the rate of oxidation(30). This idea seems in accord with the observation of faster oxidation rates for thinner films, where the $Si-SiO_2$ interface is kinetically most important, and some direct evidence for an enhanced rate of oxidation for tensile loaded Si has been presented (31). However, while there seems to be qualitative agreement with the model, quantitative scaling of the oxidation rate with σ_i is not found (32,33) and the predicted orientation dependence for the stress is not observed (18).

From Figure 6, it is seen that the intrinsic stresses for the (100), (110) and (311) Si orientations are near to each other and larger than the stress in the (111) surface. The order for oxidation rate (30,32,33) at the outset of oxidation is:

$$(110) > (111) > (311) > (100)$$

However, after several tens of nm SiO_2 growth, the order changes to:

$$(111) > (110) > (311) > (100)$$

The initial oxidation regime scales qualitatively with the number density of Si atoms in the various Si orientations, but after this regime, the change in order may be a result of the reduced compressive stress in the SiO_2, since the scaling then appears to be in the order of smaller stress higher oxidation rate (33).

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Since the initial oxidation rate does not scale quantitatively

with the number density of Si atoms, and a crossover in rate

order occurs for greater film thicknesses, a role for stress in

the oxidation mechanism can be envisaged, but it should be clear

that any definitive statements about the role of σ_i on Si

oxidation kinetics requires further investigation.

Impurity Effects on Si Oxidation

It has long been recognized (6,7) that a variety of

impurities can alter the rate of Si oxidation, the mechanism for

oxidation, and in many cases the resultant interfacial Si-SiO$_2$

electronic properties. One difficulty with the detailed

investigation of these effects is that the chemical analyses used

to identify and quantify many of the affecting impurities is far

less sensitive to the impurity than is the electronic property or

oxidation rate which is altered as a result of the presence of an

impurity. However, while the oxidation rate and electronic

effects are sensitive, they are not specific and thus there has

been great difficulty in establishing clear cause and effect

relationships. A similar situation surrounds our understanding

of the details of the cleaning process of semiconductor surfaces.

Virtually all common semiconductors are subjected to wet and/or

dry chemical processes prior to commencing the device fabrication

process (34-36). This exposure is usually termed "cleaning" and

the intent is to remove any impurities. However, it is well

known that for many of the cases examined, some impurities are

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indeed removed but often impurities are merely replaced. The success of such a cleaning process relies on the innocuous nature of replacement impurities.

Some recent research in the area of impurities and impurity effects suggests that sensitive analytical techniques applied during the cleaning process, so called "in-situ" analysis should prove useful in elucidating the area of semiconductor surface cleaning and the role of impurities (7,8,37). Among the techniques explored and herein reported are in-situ ellipsometry and in-situ contact angle used in the solution cleaning environment of Si.

In-situ Solution Techniques

A. Ellipsometry. Ellipsometry is known to be sensitive to submonolayer coverage of a surface (38). The measurables in ellipsometry are the amplitude change in the light upon reflection, Ψ, and the phase change, Δ. The measurables are related to the other parameters of the reflection problem as:

$$\tan\Psi\exp(i\Delta) = f(n_A, n_F, n_s, \lambda, \varphi) \qquad (6)$$

where the n's are refractive indices (which are in general complex) for the ambient, A, film, F and substrate, S, respectively and λ is the wavelength, L_F, the film thickness and φ the angle of incidence. Usually n_A, n_s, φ, and λ are known. Thus from a single measurement of Ψ and Δ, n_F and L_F are obtained assuming that n_F is real. Figure 7 shows the fused silica sample cell used for the in situ measurements. Alignment of this cell with sample vertical in the solution was a non trivial procedure

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with the details in the literature (37).

B.   Contact Angle.   The contact angle, θ, is defined by the
equilibrium of three surface tension rectors, γ_{ij}, at the solid,
S, liquid, L, vapor, V, interface as γ_{sv}, γ_{sl}, γ_{lv}:

$$\cos\theta = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \qquad (7)$$

Figure 8 shows the relationship.   Usually only γ_{lv} is known for a
liquid, so that since θ is measured only the difference $\gamma_{sv} - \gamma_{sl}$
is obtained.   Yet the wetting behavior of solids is directly
related to θ where large angles indicate hydrophobic behavior
(non wetting) and small angles hydrophilic behavior (wetting).
Most metals, oxides, and semiconductors are high energy solids
with surface tensions, γ_{sl}'s, of from 500 to 5000 dynes/cm.
Waxes and some polymers are low energy solids with surface
tensions of less than 100 dynes/cm$_x$.   Virtually all liquids,
except liquid metals, have surface tensions less than 100
dynes/cm. From these values, it can be argued on thermodynamic
grounds that virtually all liquids will wet most solids, so as to
lower the surface energy of the solid and thus yield a small,
hydrophilic θ.   It has been shown that the critical surface
tension, γ_c, obtained when $\cos\theta = 1$ and thus $\gamma_c = \gamma_{lv} = (\gamma_{sv} -
\gamma_{sl})$ is specifically related to the surface structure and
composition of a solid surface (39).

For the measurement of θ on semiconductor surfaces, during
cleaning, and with the surface protected from the atmosphere, an
inverted bubble technique (40) was adapted.   The apparatus used
for the experimental results and the experimental details are

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reported elsewhere (37). A gas bubble (N$_2$) can be released from the capillary and when held at the solid surface will establish the three phase equilibrium. It is important to realize that even though the bubble here is gas, the contact angle measured is the same as for the case shown in Figure 8 .

Results of In-situ Ellipsometric and Contact Angle Measurements

The first experimental result makes use of in-situ ellipsometry to follow the process of HF etching of SiO$_2$ on Si. The use of HF in Si technology is widespread for both the patterning and complete removal of SiO$_2$ from Si and the pre processing cleaning step to remove a contaminated or damaged native SiO$_2$ film. Furthermore, it is established that the exposure of Si to HF alters the oxidation rate of Si(7,37). The use of HF is an integral part of the successful cleaning of Si. It is anticipated that the etching process of SiO$_2$ in dilute HF should be able to be followed using in-situ ellipsometry, and Figure 9 shows the rather linear decrease in SiO$_2$ film thickness with etch time. In this experiment, it was expected that the bare Si surface would be reached. This seems not to be the case, as a minimum of about 20A SiO$_2$ film thickness is reached, and it even appears as if the oxide grows slightly. However, in order to correctly interpret these results, it must be remembered that an ellipsometric model of the film covered surface is required for the analysis of the Ψ, Δ data obtained during the etching process. Up to here, we have used model comprised of three components: air - SiO$_2$ film - Si substrate and the Ψ, Δ data is

always interpreted in terms of a calculated SiO_2 film thickness.
It is seen in Figure 9 that this model works quite well down to
about 20Å but below this SiO_2 thickness, the situation is not as
clear. Using this simple model, the SiO_2 etching first nearly
ceases and then the SiO_2 grows. Neither of these events is
entirely plausible considering what we know about the virulence
of the HF attack on SiO_2. If the ψ, Δ trajectory is tracked below
20Å as the SiO_2 film is removed, the situation becomes somewhat
clarified and this unmodeled data is shown in Fig. 10. The solid
line represents a theoretical calculation of ψ, Δ values for the
situation: air - SiO_2 film - Si substrate. The zero SiO_2 film
thickness, i.e. ψ, Δ for a bare Si surface is about 178°, 10.5°
and as SiO_2 grows, Δ decreases and ψ increases. The etch
experiment shown in Fig. 10 commenced at an SiO_2 film thickness
of 85nm with a ψ, Δ of about 103°, 15.5° and proceeds towards the
bare Si surface value with increasing ψ along the theoretical
curve (open circles). Excellent agreement is seen along this
line from 85 to about 2nm· However, near the 2nm ψ, Δ value, a
deviation from the theoretical curve is seen (triangles) with Δ
decreasing again and ψ increasing, but for ψ a much slower
increase than if the correct model included a growing SiO_2 film.
Thus, while a value of 2-3nm for SiO_2 is obtained for the ψ, Δ
data in the triangle region, the data is seen to deviate
substantially from the theoretical curve for SiO_2 on Si and hence
from the simple model for a film on a substrate. This strongly
suggests that the model is not correct and possibly that a

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different film is growing on the Si surface which traces out a different ψ, Δ trajectory.

In the effort to better determine the nature of the new film forming on the Si surface, in-situ contact angle measurements have proven useful(37). First it was observed that the contact angle, θ, on SiO_2 on Si was about 8° which indicates strong hydrophilic behavior of SiO_2 as anticipated for a high energy solid in contact with an essentially aqueous media. When θ is followed during HF in H_2O etching of SiO_2, an abrupt change from 8° to 78° occurs when the SiO_2 is thought to be removed (near 2nm SiO_2). The abrupt change from hydrophilic to hydrophobic behavior is a commonplace observation in HF treatment of a SiO_2 covered Si surface(42). However, based on what we know about the surface energy of Si, namely it is high, the bare Si surface should be hydrophilic as is SiO_2, and thus no abrupt change in θ is expected. We conclude that there is something else on the Si surface, something other than SiO_2 or bare Si. In order to elucidate the nature of the hydrophobic Si surface resulting from HF exposure, the critical surface tension γ_c was measured. For this purpose, a plot of measured $\cos\theta$ versus γ_{lv} is obtained on the Si surface in contact with a number of liquids with various γ_{lv} and all with HF. This was done using solutions of H_2O-CH_3OH all with 1% HF. γ_{lv} varied from 72 dynes/cm for pure H_2O to 23 dynes/cm for pure HF. Figure 11 shows the plot. First it is seen that the plot is not linear. This has been shown to be the case whenever H bonding between liquid and solid can occur (40)

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which is expected for H_2O-CH_3OH solutions. More importantly is the extrapolated value of γ_c = 27 dynes/cm for $\cos\theta$ = 1. A comparison with literature values of γ_c leads to the conclusion that the new film on Si is either a hydrocarbon and/or fluorocarbon species. Since F is present and indeed crucial, and F-C bonds are polar enough to cause H bonding between Si and liquid, we conclude that a fluorocarbon is adsorbed on the Si surface.

It is interesting that this fluorcarbon film on Si renders the surface hydrophobic thereby likely precluding much foreign and potentially degrading impurities from attaching to an otherwise high energy Si surface. In addition, this treatment leads to clean MOS devices. The effect of a final HF treatment is essentially to yield the largest oxidation rate in comparison with other accepted cleaning solutions, e.g., H_2O_2, HCl, NH_4OH (8). It is not yet known why this is the case and other effects of HF have not been determined, e.g. any long term effects of residual F after thermal oxidation.

Summary

The details of the mechanism for the reaction between Si and oxidant to form an SiO_2 film is complex with many aspects: chemical, mechanical, electrical, morphological etc.. Many reviews on silicon oxidation have treated the problem in detail. The present paper focuses on two very recent results, namely mechanical intrinsic film stress implications and impurity

effects on the oxidation mechanism. For these new studies, novel techniques were used and are in themselves interesting means to study surface films. The results, while by no means have settled the major issues, have helped to gain further insight into the important problem of the mechanism for Si oxidation.

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List of Figures

SiO₂ FILM PROPERTIES, F(T), VERSUS OXIDATION TEMPERATURE, T_{ox}
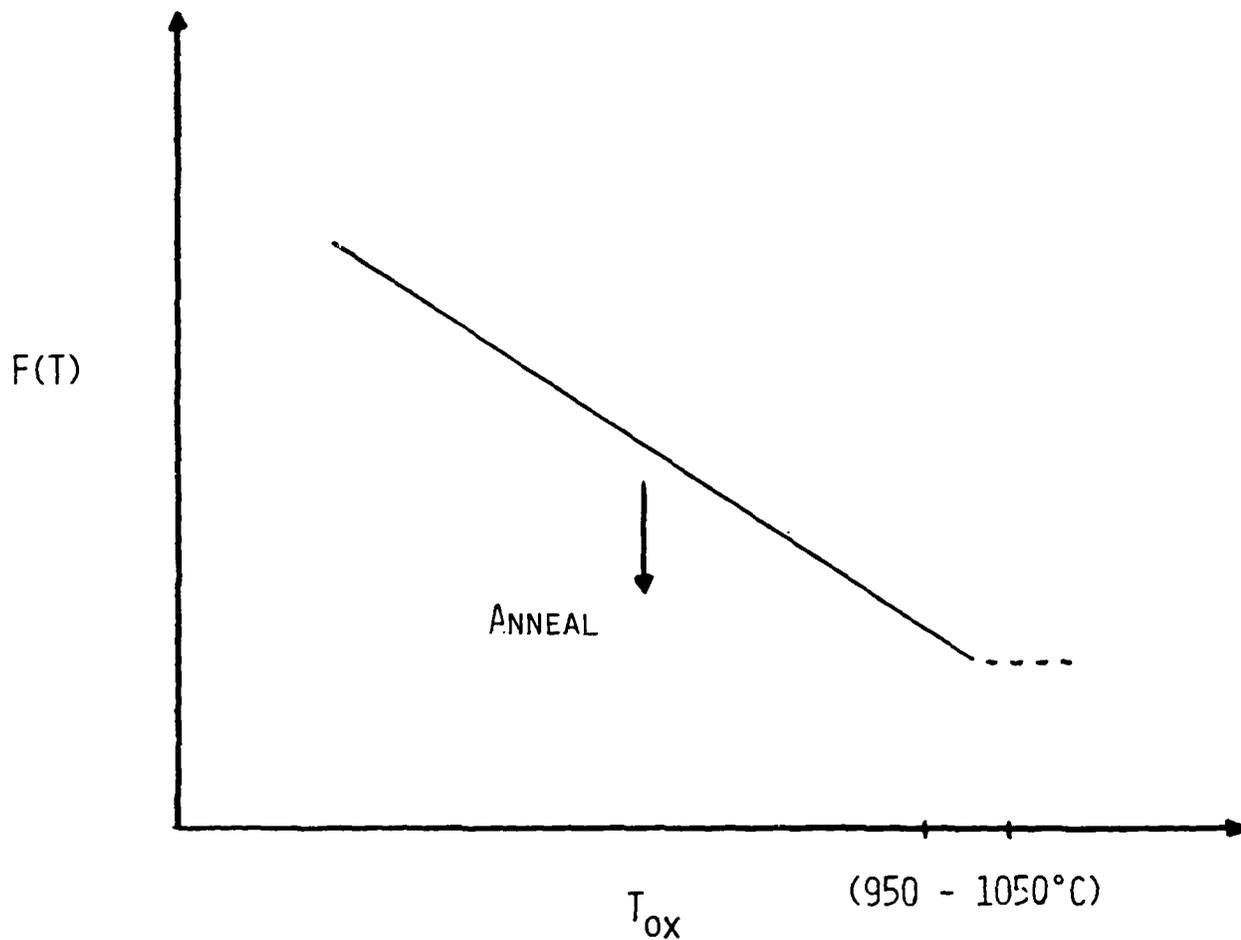
F(T)	
INTRINSIC STRESS	$\tilde{\sigma_i}$
DENSITY	ρ
REFRACTIVE INDEX	N
FIXED OXIDE CHARGE	Q_F
INTERFACE TRAPPED CHARGE	Q_{IT}

Fig 1.

laser

BS_1

prism

M_1

M_2

BS_2

screen

sample

M_3

translation stage

Fig 2

(100) Si-SiO$_2$

—●— TOTAL FILM STRESS
—○— THERMAL EXPANSION STRESS

STRESS (10^9 dyn/cm^2)

OXIDATION TEMPERATURE (°C)

Fig. 3

Fig 4

SiO$_2$ FLOW

COMPRESSIVE
STRESS

Si

Fig 5

Fig.

Fig. 5
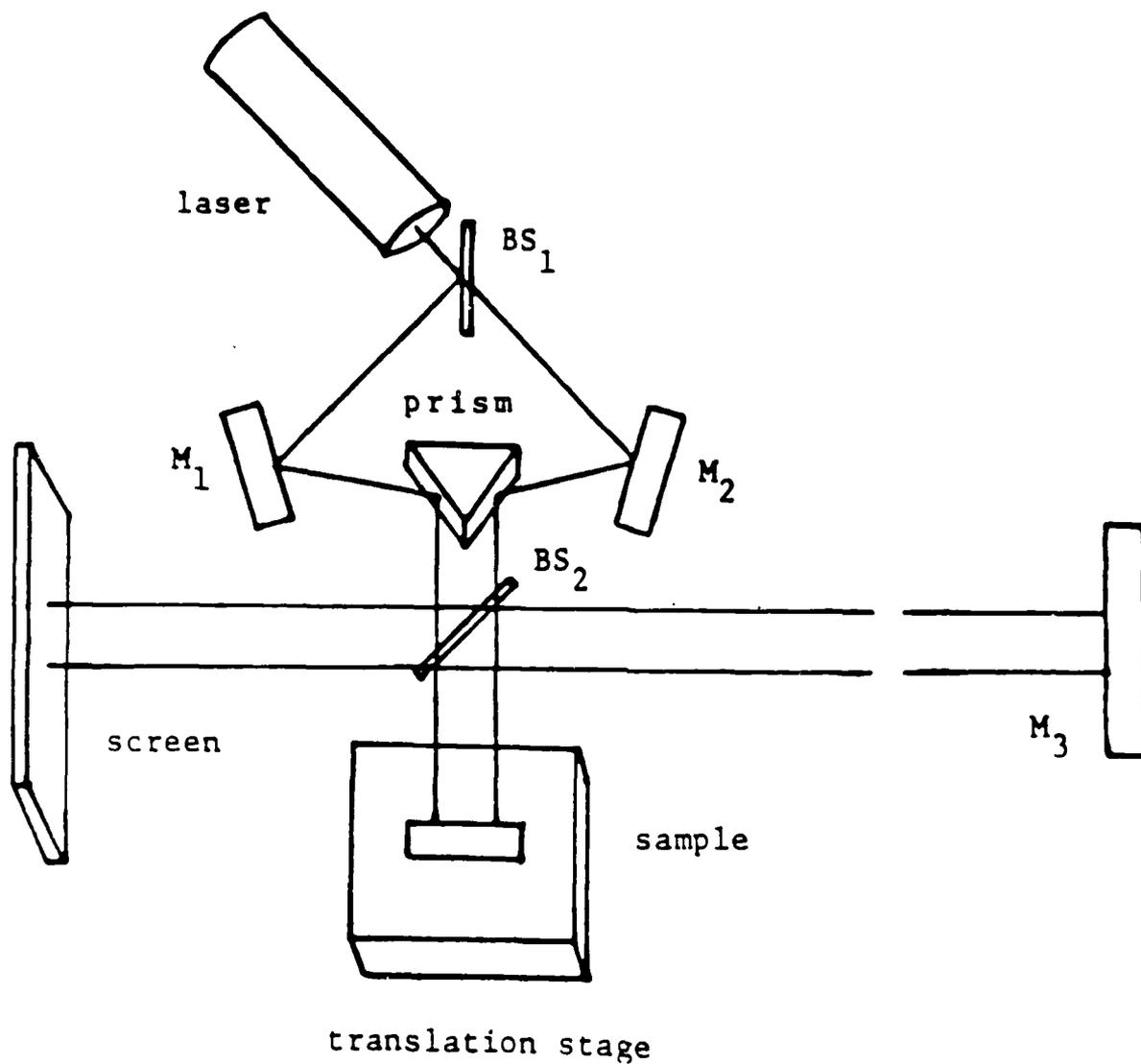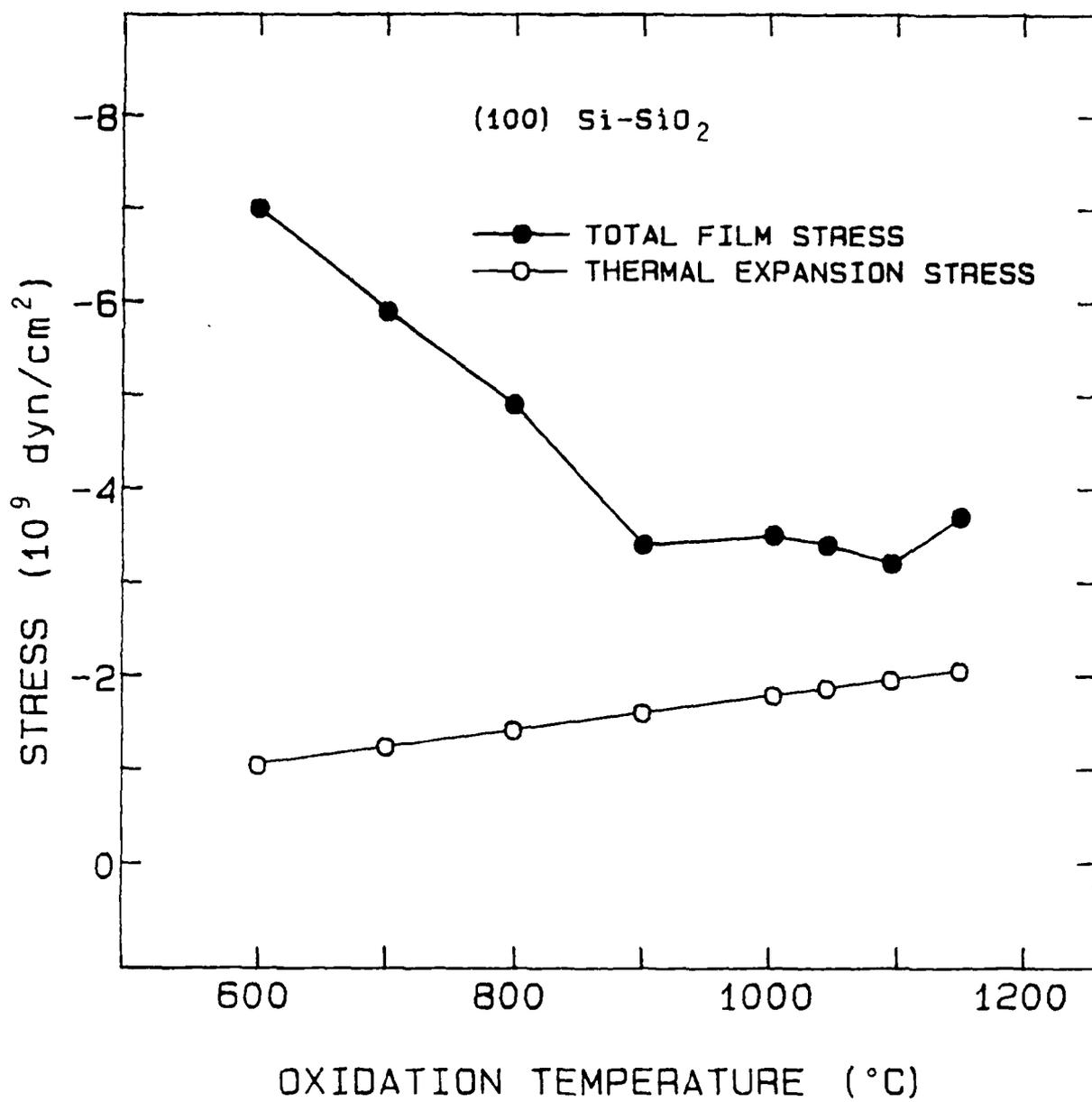
Fig. 8

Fig. 3
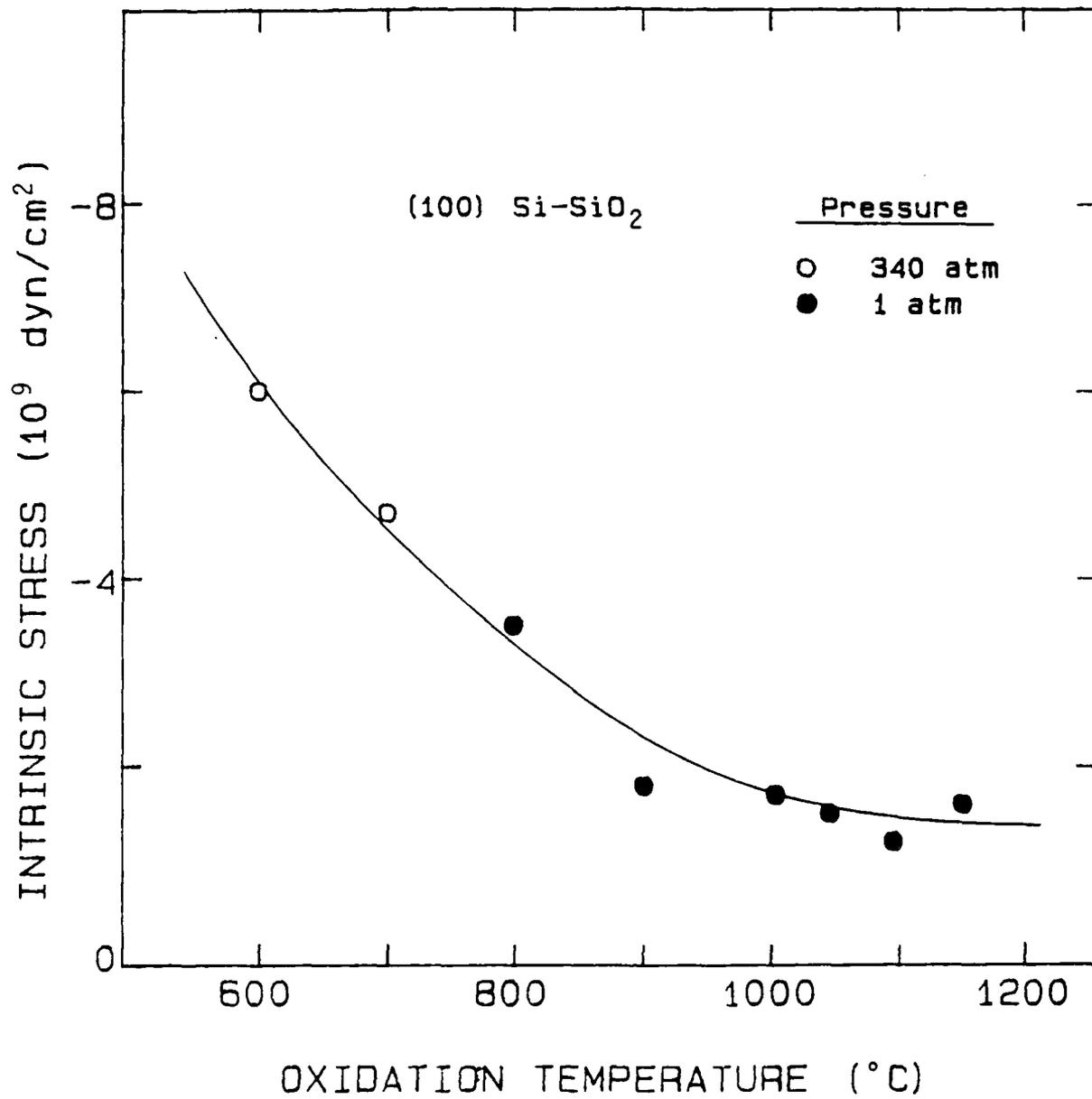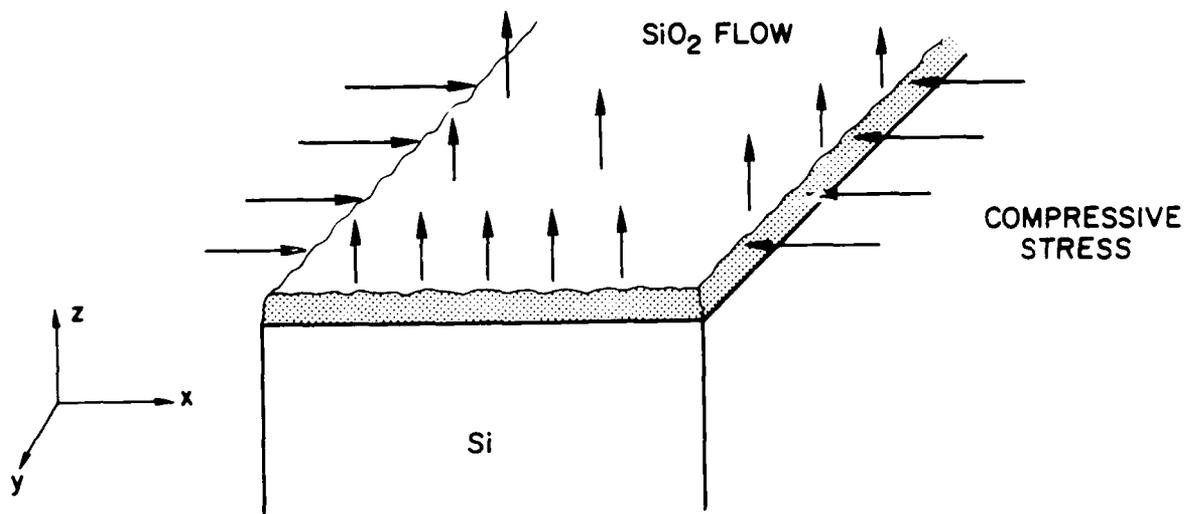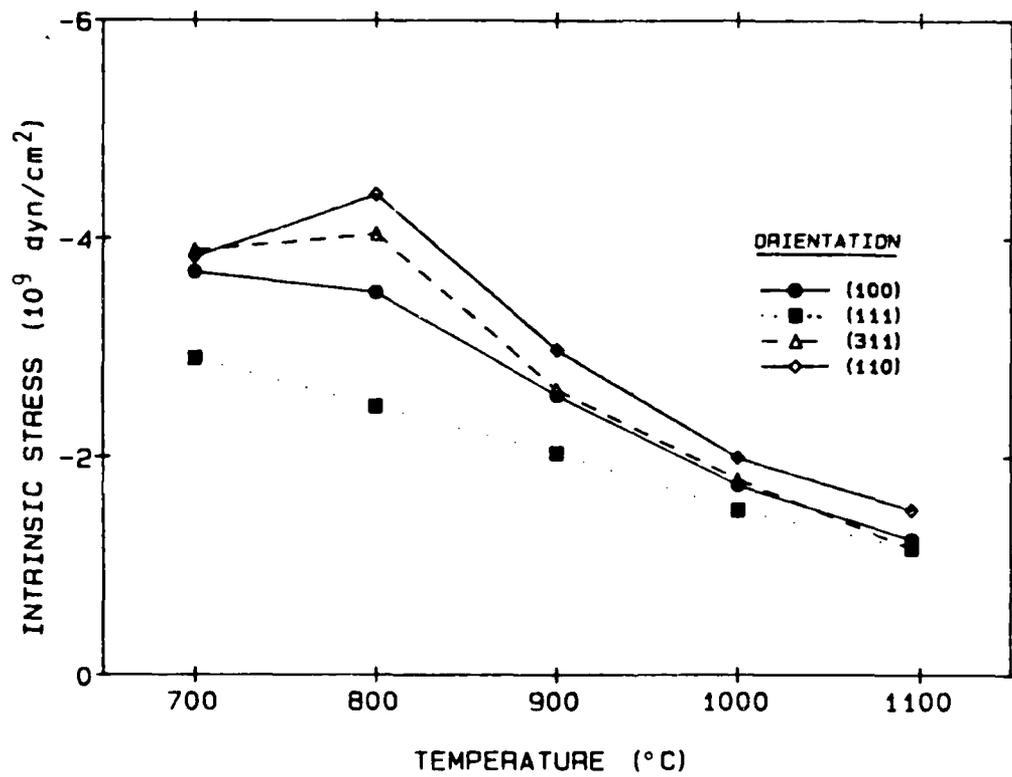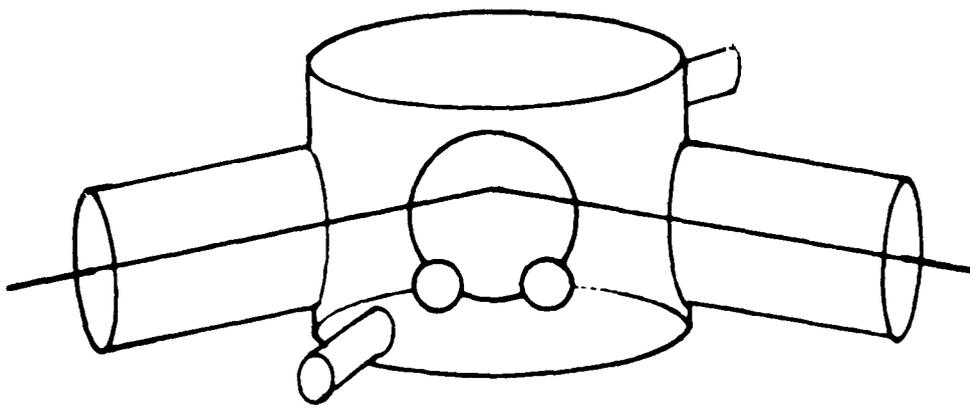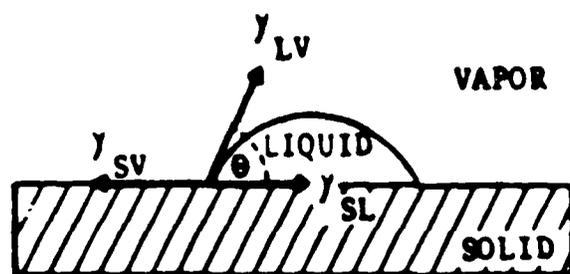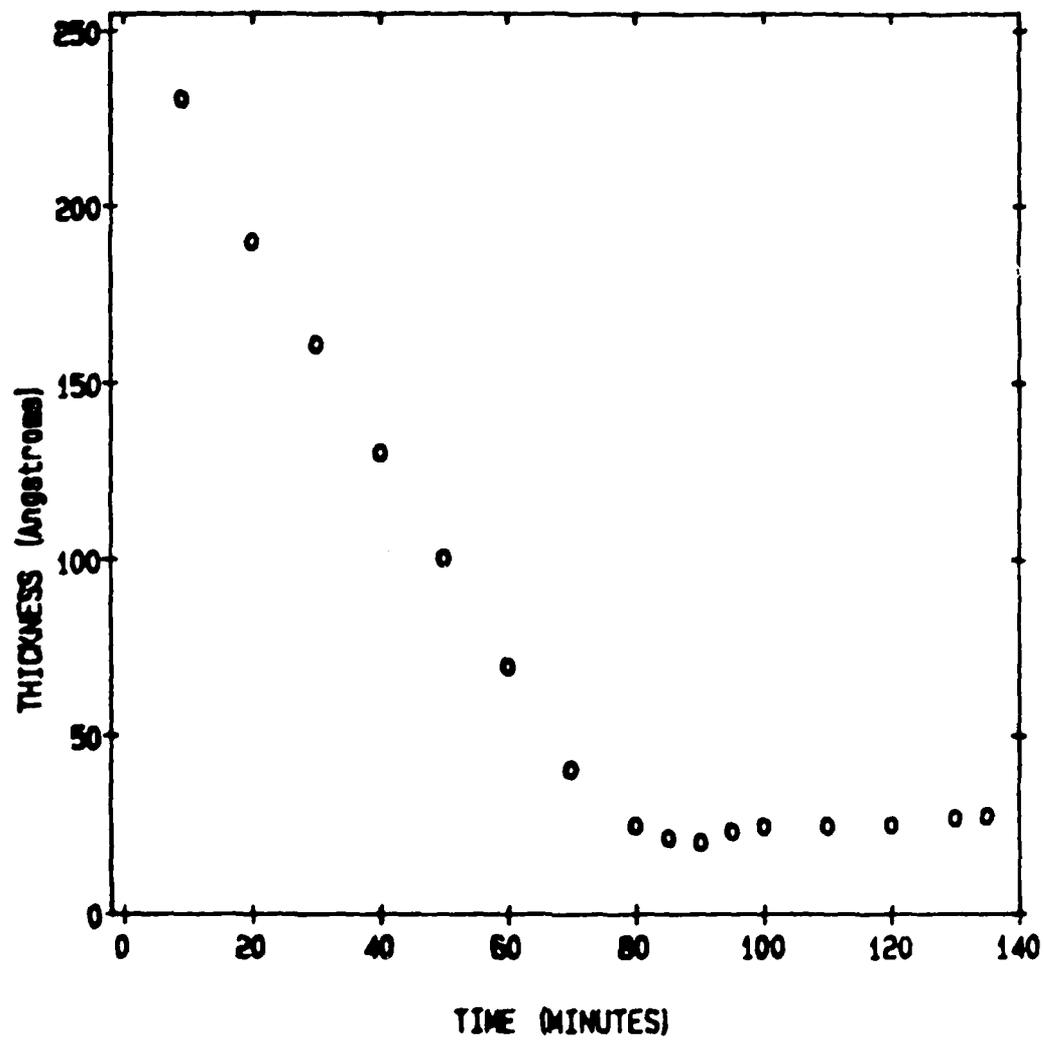
PSI vs. DELTA FOR HF ETCH EXPERIMENTS

CALCULATED ZERO
OXIDE THICKNESS

O ETCH BACK
△ LAYER GROWTH
— — THEORETICAL
CURVE

EXPERIMENTAL
MINIMUM OXIDE
THICKNESS: 2nm

LAYER
GROWTH

INITIAL OXIDE
THICKNESS: 85nm

ETCHING

DELTA (DEGREES)

PSI (DEGREES)

Fig

COS THETA

LV SURF. TENS. (dynes/cm)
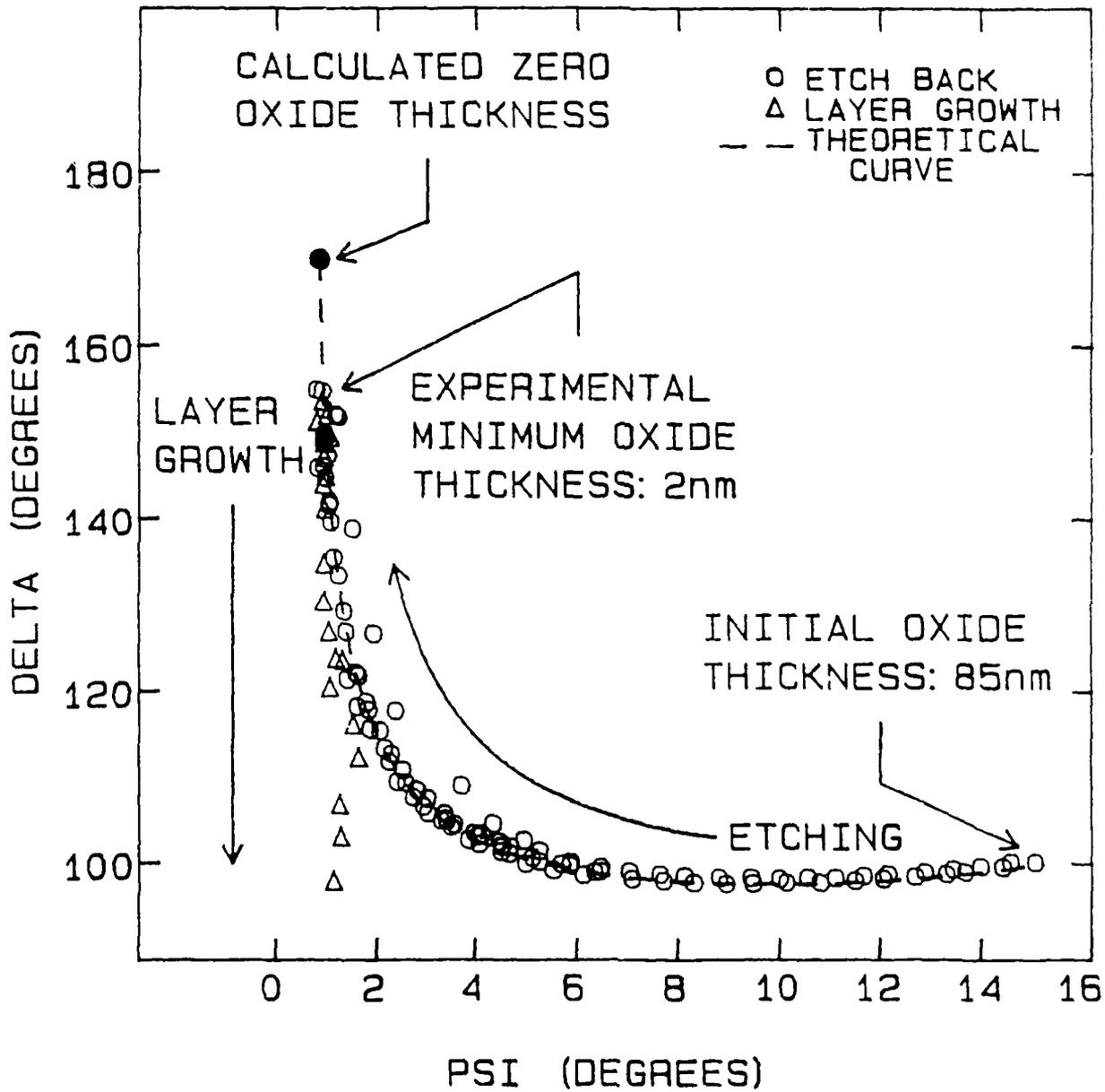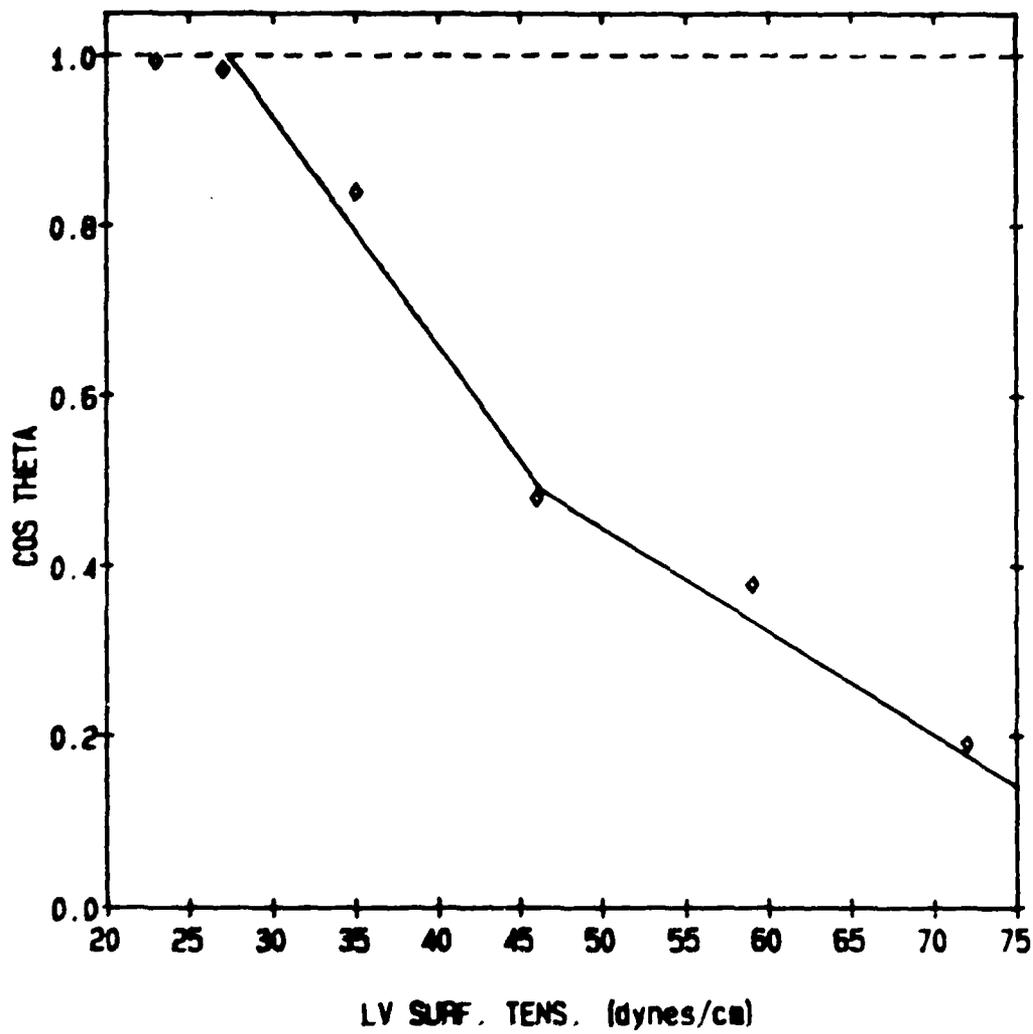
Fig 1

END

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MARCH, 1988

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